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Theoretical Study on Stability and Properties of NC_2O Isomers

Guang-tao Yu, Yi-hong Ding, Xu-ri Huang,* Hong-tao Bai, and Chia-chung Sun

State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, People's Republic of China

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The structures, energetics, spectroscopies, and stabilities of the doublet NC_2O radical are explored at density functional theory and ab initio levels. Nine minimum isomers are located connected by 22 interconversion transition states. At the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d)+ZPVE level, the lowest-lying isomer is bent NCCO **1** (0.0 kcal/mol) with $^2A'$ state followed by bent isomer CNCO **2** (16.7). Two isomers (**1** and **2**) and another high-lying species CCNO **4** (99.4) with bent structure are considerably stabilized by a barrier of at least 20 kcal/mol. All of the three isomers should be experimentally or astrophysically observable. This result is consistent with their indication of neutralization−reionization mass spectrometry experiments. Also, the calculated spectroscopic properties and bond distances of known NCCO **1** are consistent with recent experimental observations and theoretical studies. The bonding natures of the isomers **1**, **2**, and **4** are analyzed. Their molecular properties including the heats of formation, adiabatic ionization potentials, and adiabatic electronic affinities are calculated at the higher levels G3//B3LYP, G3(MP2)//B3LYP, QCISD, and CCSD(T) (single-point). Possible formation strategies of the isomers **1**, **2**, and **4** in laboratory and space are also discussed in detail.

1. Introduction

Carbon-, nitrogen-, and oxygen-containing compounds are very important in various aspects. One particular interest is their possible role in astrophysical chemistry. It is known that the fragments C_2, CN, CO, and NO have been detected in interstellar space,[1] and their direct addition may possibly lead to the formation of several NC_2O isomers, presumably as NCCO, CNCO, CCNO, and CCON. Thus, the NC_2O radical should be of interstellar interest. Furthermore, it is well-known that the reaction of the triplet C_2 radical with nitric oxide has been investigated by many investigators,[2] and it can be seen as one of the important reactions in combustion and the nitric oxide reburning processes. Then the NC_2O radical can also be recognized as an important intermediate in combustion processes. In addition, the NC_2O radical is a potential species in atmospheric chemistry.[3] In view of the significance of the NC_2O radical, extensive experimental and theoretical investigations have been carried out on the NCCO isomer.[4−7] It has been established that the NCCO radical is the major product in gas-phase photodissociation of carbonylcyanide ($CO(CN)_2$) by photofragment translational energy spectroscopy.[4] Very recently, Sumiyoshi et al.[5] obtained the pure rotational spectrum of the NCCO radical by Fourier transform microwave spectroscopy and the experimental results are also supported by high-level ab initio calculations. Imamura and Washida[6] have determined the rate constant of the $NC_2O + O_2$ reaction. Furthermore, a large number of theoretical studies have covered the structures and spectroscopies of the NCCO radical.[5,7]

In contrast to NCCO, other isomers of the NC_2O radical have been paid much less attention. Combined with ab initio calculations, the neutralization−reionization mass spectrometry experiment[7a] revealed the existence of three bent NC_2O isomers, i.e., NCCO, CNCO, and CCNO as stable species in the diluted gas phase. The structures and relative energies of the three isomeric species were calculated at the lower MP3/6-31G(d)//HF/6-31G(d)+ZPVE level. However, such structural deduction from the mass spectrometry experiment must remain ambiguous due to the possible interconversion between various structures. For example, it cannot exclude contributions of the structures NCOC and CCON, particularly because this experiment cannot cover the picture of cyclic structures. Furthermore, the kinetic stability of the three species toward isomerization and dissociation is still uncertain.

Therefore, in view of the possible existence in interstellar space yet rather limited isomerization knowledge of the important NC_2O radical, we decide to carry out a detailed theoretical study on its potential energy surface. We want to resolve the following problems: (1) Besides the known NCCO, are isomers CNCO and CCNO kinetically stable enough to allow for laboratory or interstellar observation as their indication of mass experiment? (2) Does it have other linear or cyclic ground isomers that possess considerable kinetic stability to allow experimental and astrophysical detection? (3) What is the bonding nature of the relevant isomers?

In addition, another purpose of the present paper is to evaluate the important themochemical characteristics for the relevant isomers of the NC_2O radical including the adiabatic ionization potentials, adiabatic electronic affinities as well as their heats of formation, which could better aid in their future experimental characterization.

2. Computational Methods

Computations are carried out using the Gaussian 98[8] and MOLCAS 5.2[9] (for CASSCF and CASPT2) program packages. The optimized geometries and harmonic vibrational frequencies of the local minima and transition states are obtained at the Becke three parameter Lee−Yang−Parr (B3LYP)/6-311G(d) theory level. Single-point calculations are performed at the CCSD(T)/6-311G(2d) level using the B3LYP/6-311G(d) optimized geometries. To confirm whether the obtained transition

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* To whom correspondence should be addressed.

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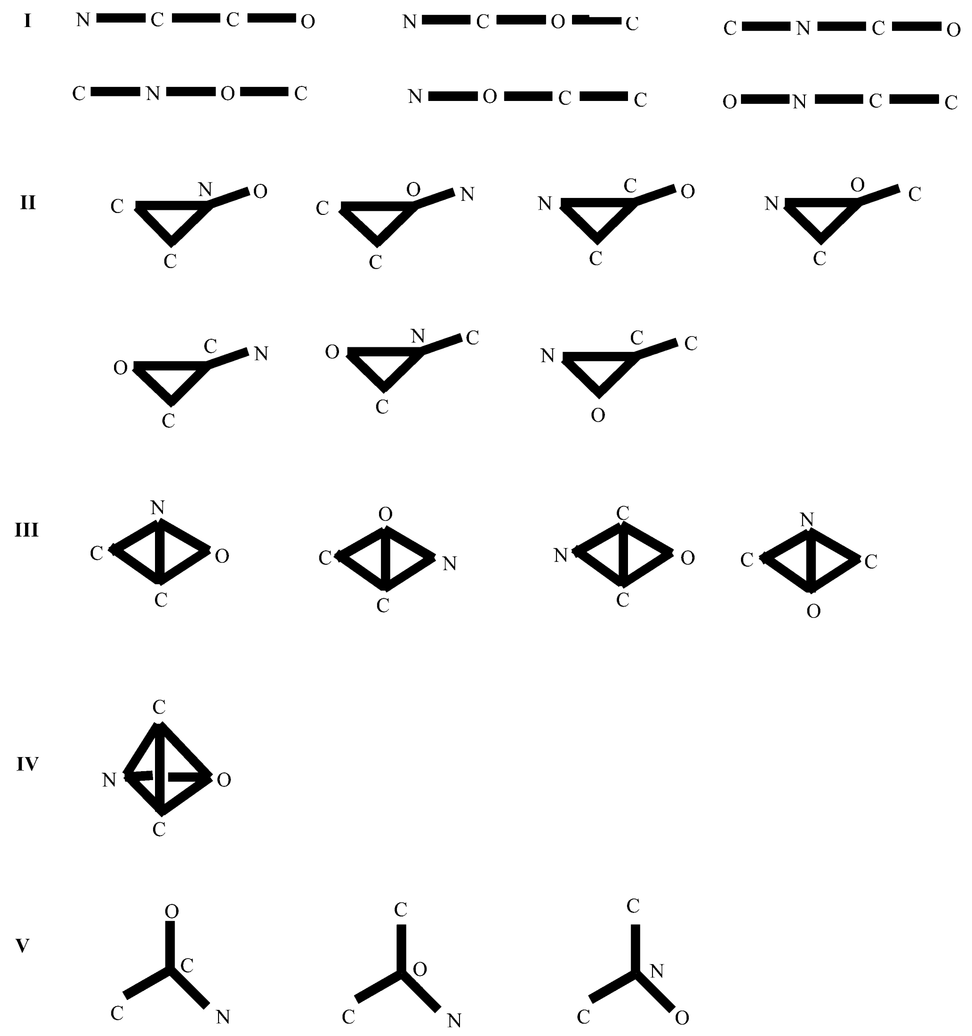


Figure 1. Scheme for isomeric species search.

states connect the right isomers, the intrinsic reaction coordinate (IRC) calculations are performed at the B3LYP/6-311G(d) level. The structures, frequencies, and energetics of the relevant species are further calculated at the G3//B3LYP, G3(MP2)//B3LYP, QCISD/6-311G(d), and CCSD(T)/6-311+G(2df) (energy only) levels. The zero-point vibrational energies (ZPVE) at the 6-311G(d)-B3LYP and QCISD levels are also included for energy correction. The multireference properties of the relevant structures are checked by additional CASPT2(11,11)/cc-pVDZ// complete active space self-consistent field (CASSCF)(11,11)/ cc-pVDZ calculations. For conciseness, the levels CCSD(T)/ 6-311G(2d)//B3LYP/6-311G(d)+ZPVE, CCSD(T)/6-311+G(2-df)//QCISD/6-311G(d)+ZPVE, and CASPT2/cc-pVDZ//CASSCF(11,11)/cc-pVDZ are simplified by CCSD(T)//B3LYP, CCSD(T)//QCISD, and CASPT2//CASSCF. Furthermore, the thermochemical quantities of the relevant species including the heats of formation, the adiabatic ionization potentials, and adiabatic electronic affinities are computed at the CCSD(T)/6-311+G-(2df)//QCISD/6-311G(d)+ZPVE, G3(MP2)//B3LYP, and G3// B3LYP levels.

3. Results and Discussions

For such a small system, it is desirable to include as many isomeric forms as possible. The isomeric search follows the scheme (Figure 1): Chainlike [formed from (CC, NO) and (CN, CO) molecule-radical pairs], three-membered ring [from the perpendicularlike attack between (CC, NO) and (CN, CO) pairs], four-membered ring [from CCNO and CNCO rings], and all-closed species.

For conciseness, the results are organized as follows. The optimized geometries of the NC_2O isomers are shown in Figure 2. The optimized geometries of the NC_2O transition states and some important fragments are shown in Figure 3. A schematic potential-energy surface (PES) of NC_2O is presented in Figure 4. The harmonic vibrational frequencies as well as the infrared intensities, dipole moments, and rotational constants of the NC_2O species are listed in Table 1, whereas the relative energies of all species and some important dissociation fragments are collected in Table 2. The adiabatic ionization potentials (IP), adiabatic electronic affinities (EA), and heats of formation for the relevant isomers are provided in Tables 3−5, respectively.

3.1. NC_2O PES. After numerous searches, 9 NC_2O minimum isomers (**m**) and 22 interconversion transition states (**TSm/n**) are obtained at the B3LYP/6-311G(d) level. Among these, six isomers have bent structures, i.e., NCCO **1** (0.0), CNCO **2** (15.8, 16.7, 17.8, 17.3, 20.5), NCOC **3** (66.9), NCOC **3′** (84.2), CCNO **4** (100.8, 99.4, 99.4, 99.5, 98.2), and CCON **5** (155.4). The isomers **1**, **2**, **3**, and **4** have C_s symmetry in $^2A'$ electronic state, whereas the species **3′** and **5** are of C_1 symmetry. The linear forms of NCCO, CNCO, and CCNO each have imaginary frequencies at the B3LYP/6-311G(d) level. In fact, they are associated with the interconversion of the isomers **1**, **2** and **4**, respectively. They are thus denoted as **TS1/1**, **TS2/2**, and **TS4/4**, respectively, as shown in Figure 3. In addition, at the B3LYP/

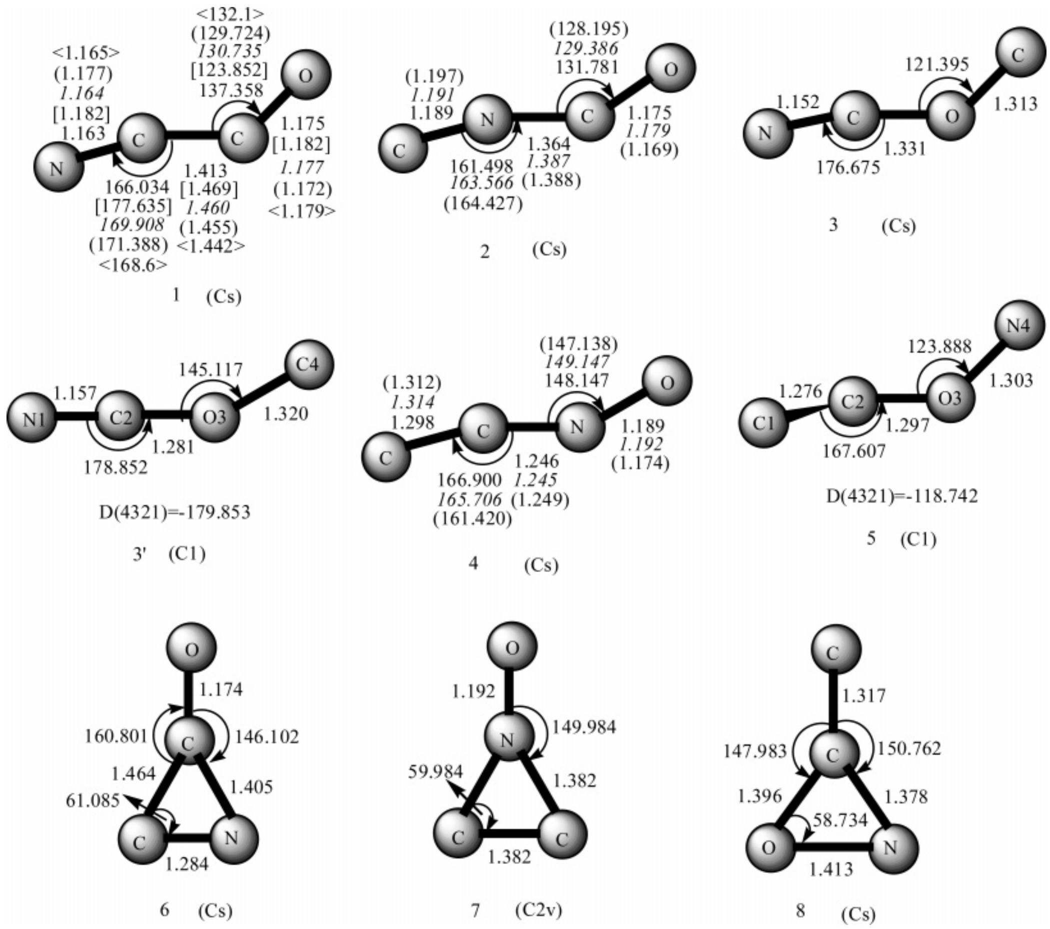


Figure 2. Optimized geometries of NC_2O isomers at the B3LYP/6-311G(d) level. The values in italics are at the QCISD/6-311G(d) level, those in parentheses are at the CASSCF(11,11)/cc-pVDZ level, and those in square brackets are at the MP2/6-311G(d) level, respectively. For the isomers **1**, the values in angle brackets are at the RCCSD(T)/core/cc-pCVTZ level. Bond lengths are in angstroms and angles in degrees.

6-311G(d) level, the $^2A''$ excited-state structure in C_s symmetry of **3** has one imaginary frequency (102i cm^{-1}). So we optimized the structure in a lower symmetry (C_1), which leads to the asymmetric species **3′** with slightly lower energy (0.5 and 0.3 kcal/mol, respectively, at the B3LYP/6-311G(d) without and with ZPVE inclusion). The first, second, third, fourth, and fifth values in parentheses are relative energies with reference to isomer **1** (0.0, 0.0, 0.0, 0.0, 0.0) at the CCSD(T)//B3LYP, CCSD(T)//QCISD, G3//B3LYP, G3(MP2)//B3LYP, and CAS-PT2//CASSCF levels. As is shown in Table 2, the isomers NCCO **1** and CNCO **2** are lower in energy than all of the other chainlike species because they possess the "best" radical−molecule combination, i.e., the stable CN radical bonds to the very stable CO molecule at its C site. The isomers **1** and **2** are also the two lowest-lying forms of all of the NC_2O isomers.

The isomers **6** (30.9), **7** (121.0), and **8** (137.4) are consistent with the three-membered ring descriptions. The species **6** and **7** both have a CCN ring with the respective exocyclic CO and NO bonding, whereas isomer **8** has a CNO ring with exocyclic CC bonding. The isomers **6** and **8** have $^2A'$ and $^2A''$ states, respectively, whereas the species **7** has a $^2B_2$ state with C_{2v} symmetry. The isomer **7** may be considered as product from the attack of O atom at the cyclic C_2N. The remaining postulated structures in Figure 1 cannot be located as minima on the PES, i.e., four-membered ring, closed tetrahedral-like, and branched-chain forms.

To discuss the kinetic stability, one needs to consider various isomerization and dissociation pathways as many as possible. For simplicity, the details of the obtained 22 transition states are omitted. As shown in Figure 4, we can see that the three isomers **1**, **2**, and **4** may be of our great interest with considerable kinetic stability. Interestingly, for isomers **1** and **2**, the least dissociation barriers govern the stability of them, whereas species **4** is determined by the smallest isomerization barrier. At the higher CCSD(T)//QCISD level, the isomers **1**, **2**, and **4** have the kinetic stability of more than 20 kcal/mol as 26.8 (**1** → **9**), 21.0 (**2** → **9**), and 29.2 (**4** → **7**), respectively, as can be deduced from Figure 4. Note that the transition state **TS1/9** governing kinetic stability of the isomer **1** is obtained at the MP2/6-311G(d) level since it cannot be located at the B3LYP/6-311G(d) level. Moreover, despite numerous attempts, the direct dissociation transition state of CCNO **4** to fragments **10** C_2+NO cannot be obtained at all of the 6-311G(d)-B3LYP, MP2, and QCISD levels, optimization of which always leads to the fragments. This suggests that the dissociation of CCNO **4** to **10** may most probably proceed without any transition state.[10]

Existence of the other isomers is less likely due to their higher energy and much smaller kinetic stability. At the CCSD(T)//B3LYP level, the least isomerization barriers of the remaining species **3**, **5**, **6**, **7**, and **8** are 3.9 (**3** → **9**), 11.9 (**5** → **8**), 2.7 (**6** → **1**), 8.5 (**7** → **4**), and 9.4 (**8** → **1**) kcal/mol, respectively.

3.2. Bonding Properties of NCCO 1, CNCO 2, and CCNO 4. We now analyze the structural and bonding properties of the three kinetic stability species **1**, **2**, and **4** mainly based on the B3LYP results. Generally, for such a small species, the molecular orbital is highly delocalized, making the structural description difficult. Here, we simply describe the "formal"

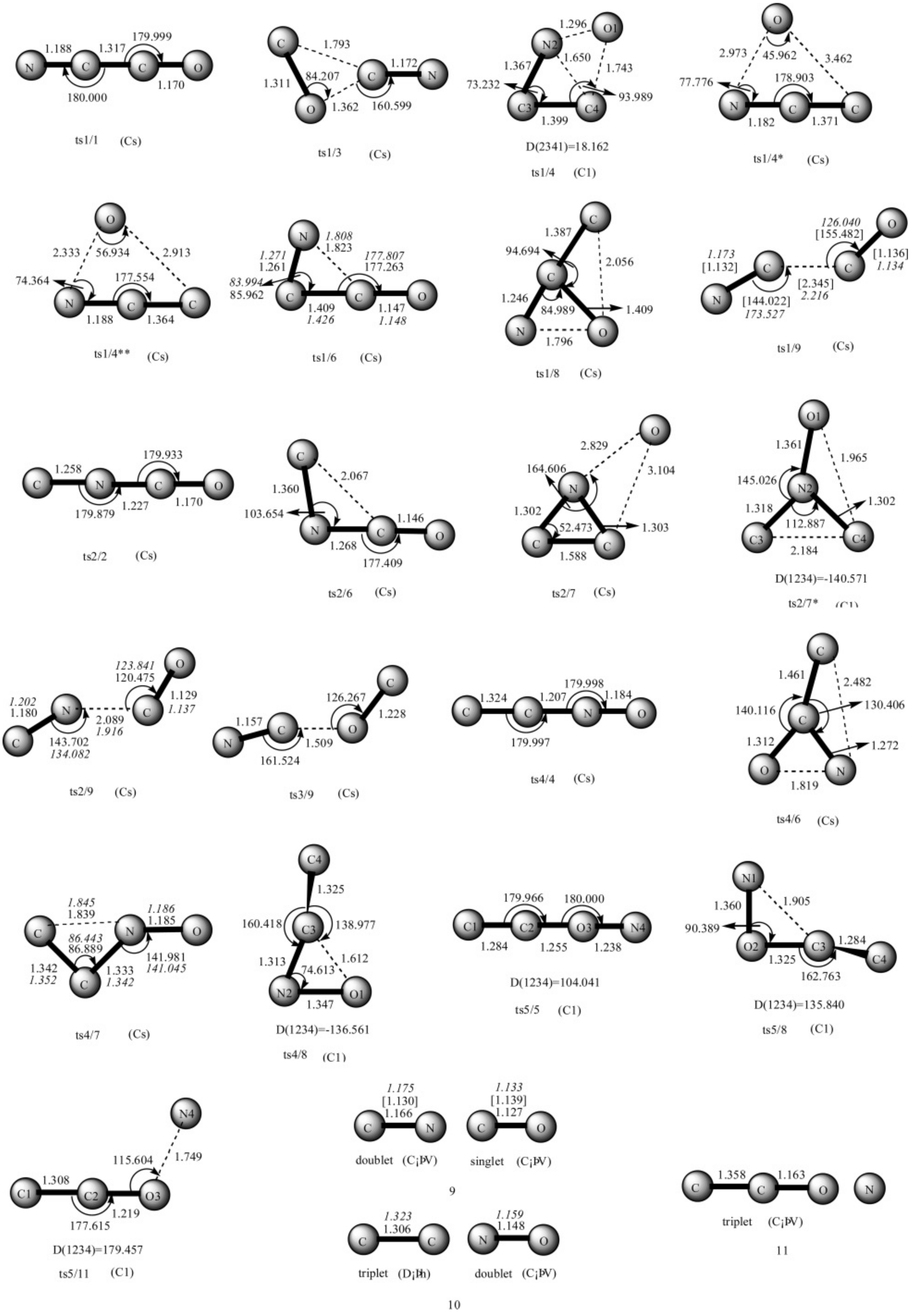


Figure 3. Optimized geometries of NC_2O transition states and important fragments at the B3LYP/6-311G(d) level. The values in italics are at the QCISD/6-311G(d) level, and those in square brackets are at the MP2/6-311G(d) level, respectively. Bond lengths are in angstroms and angles in degrees.

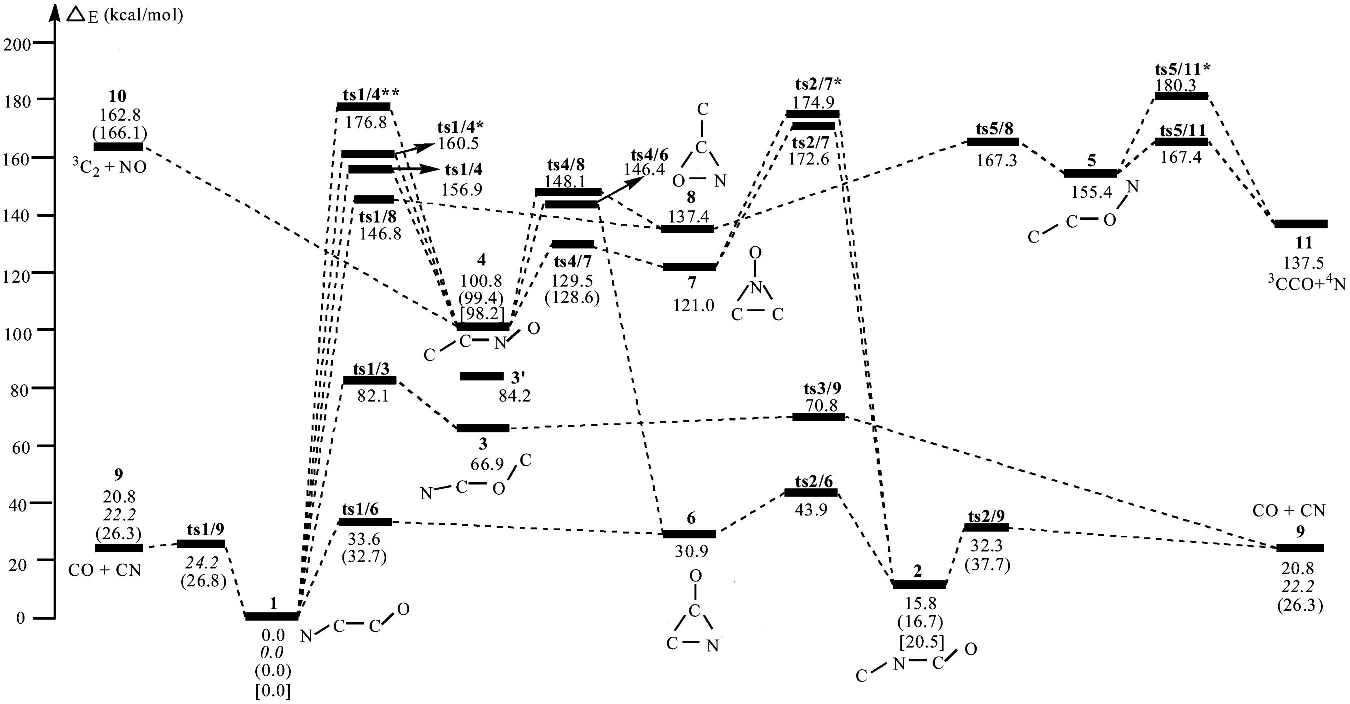


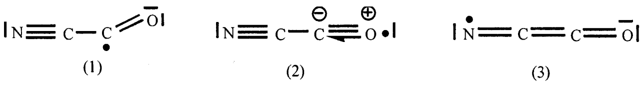
Figure 4. Schematic potential-energy surface of NC_2O at the CCSD(T)/6-311G(2d)//B3LYP/6-311G(d)+ZPVE level. The relative values in parentheses are at the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d)+ZPVE level, the values in brackets are at the CASPT2/cc-pVDZ//CASSCF-(11,11)/cc-pVDZ level, and the values in italics are at the CCSD(T)/6-311G(2d)//MP2/6-311G(d)+ZPVE level.

TABLE 1: Harmonic Vibrational Frequencies (cm^{-1}), Infrared Intensities (km/mol) (in Parentheses), Dipole Moment (Debye), Rotational Constants (GHz), and $\langle S^2\rangle$ Values of NC_2O Structures at the B3LYP/6-311G(d) Level[a]

species	frequencies (infrared intensity)	dipole moment	rotational constant	$\langle S^2\rangle$ value for UHF
NCCO 1	221(7) 277(11) 566(2) 813(4) 1967(201) 2222(17)	1.0900	243.35787, 4.75619, 4.66501	
NCCO 1[b]	221(8) 292(8) 598(2) 814(29) 2008(130) 2389(108)	1.2236	163.98818, 4.78169^B, 4.64621^C	0.9487
NCCO 1			4.71395[c]	
NCCO 1 (expt.)			4.7359[d]	
NCCO 1[e]	205(9)[e] 271(9)[e] 562(2)[e] 795(30)[e] 1939(135)[e] 2293(1333)[e]		178.470[f], 4.789[f], 4.664[f]	
CNCO 2	181(2) 216(3) 600(7) 893(33) 1928(270) 2046(223)	0.5826	205.88100, 5.28912, 5.15664	
CNCO 2[b]	173(1) 195(3) 605(7) 912(85) 1907(215) 2080(307)	0.8236	177.99221, 5.26870, 5.11723	0.7916
NCOC 3	234(9) 417(9) 578(1) 904(11) 1189(243) 2356(29)	1.3741		
NCOC 3′	123(6) 470(9) 474(9) 884(32) 1372(358) 2373(201)	1.5456		
CCNO 4	193(7) 220(7) 435(2) 995(27) 1712(4) 1954(876)	1.7434	432.36225, 5.03161, 4.97372	
CCNO 4[b]	178(5) 216(7) 400(9) 988(30) 1668(2) 1887(1122)	1.6933	477.59062, 4.97208, 4.92085	0.9376
CCON 5	165(20) 207(18) 468(3) 883(39) 1073(12) 1929(38)	2.6874		
O-cCCN 6	481(17) 558(20) 655(30) 885(8) 1579(14) 2028(323)	0.3643		
O-cNCC 7	465(141) 546(9) 553(97) 897(3) 1356(18) 1759(244)	0.0211		
C-cCNO 8	241(23) 386(4) 640(50) 819(85) 1097(44) 1745(75)	0.9125		

[a] For the relevant isomers, the QCISD/6-311G(d) values are included also. [b] At the QCISD/6-311G(d) level. [c] Indicate the averaged values of B and C, i.e., (B + C)/2, at the QCISD/6-311G(d) level, from the present work. [d] Reference 5. [e] At the QCISD/6-31G(d) level, from ref 7b. [f] At the RCCSD(T)/core/cc-pCVTZ level, from ref 5.

valence structures of each relevant isomer based on the bond distances and spin density distribution without performing valence bond theory calculations. The lowest-lying isomer NCCO **1** has the $^2A'$ electronic state. Its calculated CN bond value (1.163 Å) is very close to the C≡N (1.149 Å from HC≡N[11]) bond value. Its CO bond length (1.175 Å) is closer to the C═O bond length (1.200 Å) than to the C≡O (1.127 Å) bond length. The distribution of the spin density is 0.179, −0.013, 0.568 and 0.266e for N, C, C and O, respectively. Thus, the isomer **1** can be viewed as resonating between three forms:



The symbols "•" and "|" denote the single electron and lone-pair electrons, respectively. The form (1) may contribute the most and (3) the least. The above structural description is also supported by the natural bond orbital (NBO) analysis. Note that the symbols "+" and "−" just indicate the formal charges to describe the ionic structure of the sub-valence form (2). They do not represent the real charge distributions of the isomer **1**. As a result, structurally the low-lying form **1** can be considered as the combination between doublet CN radical and singlet CO molecule.

The bent isomer CNCO **2** has the $^2A'$ electronic state. Its calculated CN bond value (1.189 Å) is closer to the C≡N (1.149 Å) bond value than to the C═N bond value (1.266 Å). Its CO bond length (1.175 Å) is closer to the C═O bond length (1.200 Å) than to C≡O (1.127 Å) bond length. The distribution of the spin density is 0.157, −0.026, 0.633, and 0.235e for C, N, C, and O, respectively. Thus, the isomer **2** can be viewed as a resonance structure between three forms:

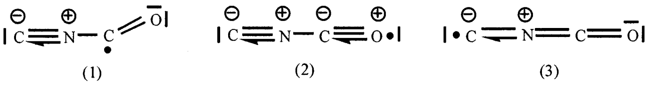


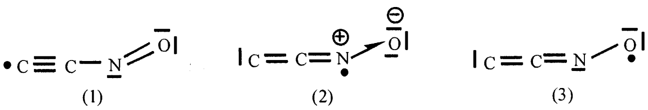
TABLE 2: Relative (kcal/mol) Energies of the NC_2O Isomers, Transition States and Important Fragments at the B3LYP/6-311G(d) and Single-Point CCSD(T)/6-311G(2d) Levels[a]

species	B3LYP[d]	ΔZPVE B3LYP[d]	CCSD(T)[e] //B3LYP[d]	total 1	QCISD[d]	ΔZPVE QCISD[d]	CCSD(T)[f] //QCISD[d]	total 2	G3// B3LYP	G3(MP2) //B3LYP	CASPT2// CASSCF (11,11)[g]
NCCO 1 ($^2A'$)[b]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CNCO 2 ($^2A'$)	16.8	−0.3	16.1	15.8	16.8	−0.6	17.3	16.7	17.8	17.3	20.5
NCOC 3 ($^2A'$)	71.5	−0.6	67.5	66.9							
NCOC 3′	85.1	−0.5	84.7	84.2							
CCNO 4 ($^2A'$)	95.6	−0.8	101.6	100.8	107.6	−1.4	100.8	99.4	99.4	99.5	98.2
CCON 5	153.6	−1.9	157.3	155.4							
O-cCCN 6 ($^2A'$)	28.2	0.2	30.7	30.9							
O-cNCC 7 ($^2B_2$)	116.5	−0.7	121.7	121.0							
C-cCNO 8 ($^2A''$)	138.7	−1.6	139.0	137.4							
CN($^2\Sigma$)+CO($^1\Sigma$) 9	37.4	−2.4	23.2	20.8	21.6	−2.8	29.1	26.3			
CN($^2\Sigma$)+CO($^1\Sigma$) 9[c]	45.5	−3.7	25.9	22.2							
CC($^{3\prime}{}_{u}{}^{-}$)+NO($^{2\prime}$) 10	175.3	−3.4	166.2	162.8	165.3	−4.0	170.1	166.1			
CCO ($^3\Sigma$)+N (^4S) 11	152.5	−3.1	140.6	137.5							
TS1/1 ($^2A'$)	4.2	−0.2	10.0	9.8							
TS1/3 ($^2A'$)	86.2	−1.4	83.5	82.1							
TS1/4	160.9	−2.2	159.1	156.9							
TS1/4* ($^2A'$)	171.2	−3.2	163.7	160.5							
TS1/4** ($^2A'$)	185.7	−3.2	180.0	176.8							
TS1/6 ($^2A'$)	34.1	−0.7	34.3	33.6	37.2	−1.2	33.9	32.7			
TS1/8 ($^2A''$)	152.1	−2.6	149.4	146.8							
TS1/9 ($^2A'$)[c]	45.0	−3.1	27.3	24.2	25.0	−2.3	29.1	26.8			
TS2/2 ($^2A'$)	28.3	−0.7	34.5	33.8							
TS2/6 ($^2A'$)	43.5	−0.6	44.5	43.9							
TS2/7 ($^2A'$)	184.4	−4.0	176.6	172.6							
TS2/7*	179.7	−2.8	177.7	174.9							
TS2/9 ($^2A'$)	41.8	−2.1	34.4	32.3	37.0	−2.5	40.2	37.7			
TS3/9 ($^2A'$)	76.6	−2.5	73.3	70.8							
TS4/4 ($^2A'$)	97.2	−1.0	104.2	103.2							
TS4/6 ($^2A'$)	157.3	−2.4	148.8	146.4							
TS4/7 ($^2A'$)	128.5	−1.3	130.8	129.5	137.1	−1.8	130.4	128.6			
TS4/8	147.8	−2.7	150.8	148.1							
TS5/5	166.7	−2.3	176.1	173.8							
TS5/8	168.4	−2.8	170.1	167.3							
TS5/11	169.7	−3.1	170.5	167.4							
TS5/11*	188.3	−3.3	183.6	180.3							

[a] For the relevant species, the values at the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d), G3//B3LYP, G3(MP2)//B3LYP, and CASPT2/cc-pVDZ//CASSCF/cc-pVDZ are listed also. The symbols in parentheses of the column denote the point group symmetry. Only the electronic states of the species that are not of C_1 symmetry are given. [b] The total energies of reference isomer **1** at the B3LYP/6-311G(d) level are −206.1427458 au, at the MP2/6-311G(d) level is −205.6138433 au, at CCSD(T)/6-311G(2d)//B3LYP/6-311G(d) level is −205.6874087 au, at CCSD(T)/6-311G(2d)//MP2/6-311G(d) level is −205.6878968 au, at the QCISD/6-311G(d) level is −205.6219434 au, at the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d) level is −205.7578663 au, at the G3//B3LYP level is −205.9908787 au, at the G3(MP2)//B3LYP level is −205.837174 au, at the CASPT2(11,11)/cc-pVDZ//CASSCF(11,11)/cc-pVDZ is −205.55532706 au, respectively. The ZPVE at the B3LYP, MP2 and QCISD level are 0.013819, 0.017334 and 0.014402 au, respectively. [c] The values are obtained at MP2/6-311G(d) level. [d] The basis set is 6-311G(d) for B3LYP and QCISD. [e] The basis set is 6-311G(2d) for CCSD(T). [f] The basis set is 6-311+G(2df) for the CCSD(T). [g] The basis set is cc-pVDZ for CASSCF and CASPT2.

Structure (1) may contribute the most with (3) the least. Thus, we may intend to suggest that isomer **2** can be obtained via the direct addition between doublet CN radical and singlet CO molecule. The above structural descriptions are also supported by the natural bond orbital (NBO) analysis.

The bent isomer CCNO **4** has the $^2A'$ electronic state. Its calculated CC bond length (1.298 Å) is close to the normal C═C (1.327 Å) bond length. Its NO bond value (1.189 Å) is very close to the N═O (1.200 Å) bond value. Its internal CN bond length (1.246 Å) is close to the C═N (1.266 Å) bond value. The distribution of the spin density is 0.419, −0.088, 0.372 and 0.297e for C, C, N and O, respectively. Thus, the isomer **4** can be viewed as resonating between three forms:



The weight of the three forms decreases from (1) to (3). It could be thought of the direct addition of between C_2 molecule and doublet NO radical.

Finally, it is clear that the first-row N and O atoms in NC_2O have much more tendency to form π-bonding, which can interpret why the cyclic structures of NC_2O are kinetically unstable.

3.3. Themochemical Properties of NCCO 1, CNCO 2, and CCNO 4. Important themochemical characteristics for radicals are the adiabatic ionization potentials, adiabatic electronic affinities as well as their heats of formation. As are presented in Table 3, the adiabatic ionization potentials (IP) of the isomers **1**, **2**, and **4** are computed at the CCSD(T)//QCISD, G3(MP2)//B3LYP, and G3//B3LYP levels, respectively. All of the three cationic species have singlet ground-state structures. It is shown that three methods predict very similar ionization potentials. When the G3//B3LYP method is used, the calculated IPs of the species **1**, **2**, and **4** are 204.1, 198.3, and 215.1 kcal/mol, respectively. It should be mentioned that the calculated adiabatic ionization potential value (201.5) of NCCO **1** at the CCSD(T)//QCISD level is the same as its previous theoretical result.[7b]

Furthermore, the adiabatic electronic affinities (EA) of the three isomers **1**, **2,** and **4** are also evaluated at the CCSD(T)//QCISD, G3(MP2)//B3LYP, and G3//B3LYP levels. As shown

TABLE 3: Calculated Adiabatic Ionization Potentials (IP) for Three Isomers NCCO, CNCO, and CCNO

Total Energy (Hartree)

species[a]	QCISD[b]	ZPVE QCISD[b]	CCSD(T)[c] //QCISD[b]	G3// B3LYP	G3(MP2) //B3LYP
$NCCO^+$ ($^1\Sigma$)	−205.3075903	10.11958	−205.4384847	−205.6655786	−205.5109826
$CNCO^+$ ($^1\Sigma$)	−205.290482	9.75961	−205.4198403	−205.6466108	−205.4928613
$CCNO^+$ ($^1\Sigma$)	−205.1143689	9.21735	−205.2600045	−205.4897282	−205.3357585

Relative Energies (kcal/mol)

level of theory	IP (NCCO)	IP (CNCO)	IP (CCNO)
CCSD(T)[c]//QCISD[b] + Δ ZPVE	201.5	196.2	213.2
G3//B3LYP	204.1	198.3	215.1
G3(MP2)//B3LYP	204.7	198.8	215.1

[a] The total energies of neutral isomers NCCO **1**, CNCO **2**, and CCNO **4** at the G3//B3LYP, G3(MP2)//B3LYP, QCISD/6-311G(d), and single point CCSD(T)/6-311+G(2df) levels as well as the ZPVE at the QCISD level are listed in footnote *b* of Table 2. The optimized geometries of the corresponding cations of the relevant NC_2O isomers at the QCISD/6-311G(d) level are shown in Figure 5 of the Supporting Information. The symbols in parentheses of the column denote the point group symmetry. [b] The basis set is 6-311G(d) for QCISD. [c] The basis set is 6-311+G(2df) for CCSD(T).

TABLE 4: Calculated Adiabatic Electronic Affinities (EA) for Three Isomers NCCO, CNCO, and CCNO

Total Energy (Hartree)

species[a]	QCISD[b]	ZPVE QCISD[b]	CCSD(T)[c] //QCISD[b]	G3// B3LYP	G3(MP2) //B3LYP
$NCCO^-$ ($^3\Sigma$)	−205.6354525	7.81547	−205.7937684	−206.0323057	−205.8781487
$CNCO^-$ ($^3A''$)	−205.5906451	7.76410	−205.7493599	−205.9869268	−205.8333335
$CCNO^-$ ($^1A'$)	−205.5394471	7.90852	−205.705076	−205.9435044	−205.7914924

Relative Energies (kcal/mol)

level of theory	EA (NCCO)	EA (CNCO)	EA (CCNO)
CCSD(T)[c]//QCISD[b]+ Δ ZPVE	23.7	12.6	67.4
G3//B3LYP	26.0	15.3	69.7
G3(MP2)//B3LYP	25.7	14.9	70.9

[a] The total energies of neutral isomers NCCO **1**, CNCO **2**, and CCNO **4** at the G3//B3LYP, G3(MP2)//B3LYP, QCISD/6-311G(d), and single point CCSD(T)/6-311+G(2df) levels as well as the ZPVE at the QCISD level are listed in footnote *b* of Table 2. The optimized geometries of the corresponding anions of the relevant NC_2O isomers at the QCISD/6-311G(d) level are shown in Figure 5 of the Supporting Information. The symbols in parentheses of the column denote the point group symmetry. [b] The basis set is 6-311G(d) for QCISD. [c] The basis set is 6-311+G(2df) for CCSD(T).

in Table 4, the three methods predict similar adiabatic electronic affinities. Considering the accuracy of the G3//B3LYP level of theory, the EA values of species **1**, **2**, and **4** are predicted to be 26.0, 15.3 and 69.7 kcal/mol, respectively. Note that the anionic $\mathbf{1}^-$ and $\mathbf{2}^-$ have triplet ground states, whereas $\mathbf{4}^-$ has singlet ground state. The discrepancy can be explained by the frontier orbital nature of the neutral species. For **1** and **2**, the unpaired single electron lies in the −CO π antibonding orbital, whereas that for **4** lies in the −CC π bonding orbital.

To get a good estimate of the enthalpy of formation of the NCCO radical, we have selected the isodesmic reaction approach with the following reaction:

$$NCCO + HCN \rightarrow C_2N_2 + HCO$$

Reliable experimental enthalpies of formation for HCN,[12a] NCCN,[12b] and HCO[12a] are available (32.4, 74.4, and 10.3 kcal/mol, respectively). Based on the calculated energies in Table 5, at the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d), CCSD(T)/6-311+G(2df)//QCISD/6-311G(d)+ZPVE, and G3//B3LYP levels, the corresponding enthalpy changes of the reaction are predicted to be 2.3, 1.5, and 1.0 kcal/mol. The corresponding enthalpy of formation for **1** is therefore predicted to be 50.0, 50.5, and 51.3 kcal/mol. It should be mentioned that the calculated enthalpy values for **1** are similar to its previous theoretical result (50.2 kcal/mol).[7b] Considering the accuracy of the G3//B3LYP theory model computing the enthalpy of formation, however, the enthalpy of formation for **1** is predicted to be 51.3 kcal/mol. The corresponding values for **2** and **3** are evaluated simply from their relative energies with respect to **1** at the same level. By the way, at the G3//B3LYP level, we have obtained 69.1 and 150.7 kcal/mol for **2** and **3**, respectively.

3.4. Interstellar and Laboratory Implications. Up to now, the fragments CN, CO, C_2, and NO have been detected in interstellar space,[1] the direct addition between CN and CO or between C_2 and NO may form the isomers **1**, **2**, and **4**. From the PES of NC_2O (in Figure 4), interestingly, the fragments −CN($^2\Sigma$) and −CO($^1\Sigma$) can associate to give NCCO **1** with a very small barrier, which is only 0.5 kcal/mol. Therefore, the formation of NCCO may actually occur easily via such an association procedure under laboratory and interstellar conditions. For the species CNCO **2**, from the PES, the fragments −NC($^2\Sigma$) and −CO($^1\Sigma$) can associate to form CNCO with a considerably higher barrier, 11.4 kcal/mol, than that to form NCCO **1**. However, the species CNCO may also be observed under the laboratory condition. Of course, for such an association barrier, the association reaction is also possible to produce CNCO in diffuse interstellar space where the temperature is high and the radiation is rich. Surely, the formation of NCCO **1** from the direct addition between CN and CO is not only thermodynamically but also kinetically more favorable than formation of CNCO **2**. Finally, CCNO **4** can be generated easily via the direct addition between C_2 and NO and can be collisionally stabilized in dense clouds. Surely, the removal of excess energy via collisions or radiation is important for the formation of

TABLE 5: Heats of Formation for Three Isomers NCCO, CNCO, and CCNO

Total Energy (Hartree)

species	QCISD[a]	ZPVE QCISD[a]	CCSD(T)[b]//QCISD[a]	G3//B3LYP
OCCN	−205.6219434	9.03742	−205.7578663	−205.9908787
HCN	−93.1997272	10.12287	−93.2658276	−93.3782456
C_2N_2	−185.2202551	10.14516	−185.3482116	−185.5734859
HCO	−113.5972548	8.17697	−113.6718612	−113.7940979

Relative Energies (kcal/mol)

level of theory	$\Delta H^0_{r,0}$ ($OCCN + HCN \rightarrow C_2N_2 + HCO$)	$\Delta H^0_{r,0}$ (OCCN)	$\Delta H^0_{r,0}$ (CNCO)[c]	$\Delta H^0_{r,0}$ (CCNO)[c]
CCSD(T)[b]//QCISD[a]	2.3	50.0		
CCSD(T)[b]//QCISD[a]+ Δ ZPVE	1.5	50.5	67.2	149.9
G3//B3LYP	1.0	51.3	69.1	150.7

[a] The basis set is 6-311G(d) for QCISD. [b] The basis set is 6-311+G(2df) for CCSD(T). [c] The corresponding values for CNCO **2** and CCNO **4** are evaluated simply from their relative energies with respect to NCCO **1** at the same level. Their relative energies with respect to **1** at the CCSD(T)//QCISD + Δ ZPVE and G3//B3LYP levels are listed in Table 2.

isomer **4**. Yet, in diffuse clouds, further arrangement of **4** to **1** and **2** is possible via the intermediate **6**.

The present theoretical studies show that three bent isomers NCCO **1**, CNCO **2**, and CCNO **4** have considerable kinetic stability and may be experimentally observable. Additionally, their previous neutralization−reionization mass spectrometry experiments also indicated that three species **1**, **2**, and **4** are stable species in the gas phase. Therefore, the three isomers are expected to have a very long lifetime once formed. For the lowest-energy species **1**, it has been characterized by experimental and theoretical studies.[4−7] As shown in Table 1, the rotational constants obtained by the present calculations agree with those determined experimentally within 1%.[5] Of course, our calculated spectroscopic properties (in Table 1) and bond distances (in Figure 2) at the QCISD/6-311G(d) level are also in good agreement with previous QCISD/6-31G(d)[7b] and RCCSD(T)/core/cc-pCVTZ[5] theoretical results. For the isomers **2** and **4**, however, they have received much less attention. In view of their potential importance, two isomers **2** and **4** are expected to obtain much more studies. Therefore, to aid future experimental and interstellar characterization, the structures, vibrational frequencies, dipole moments, and rotational constants at the QCISD/6−311(d) level, which are hitherto the most accurate values for the two isomers **2** and **4**, are provided in Figure 2 and Table 1. As shown in Table 1, the dominant vibrational bands for the isomers **1**, **2**, and **4** are 2008, 2080, and 1887 cm^{-1}, respectively, with corresponding infrared intensities of 130, 307, and 1122 km/mol. In addition, isomer **4** has a large dipole moment 1.6933 D, making it very promising for microwave detection. Furthermore, the molecular properties of three isomers **1**, **2**, and **4** including the heats of formation, the adiabatic ionization potentials and adiabatic electronic affinities are also determined. We hope that our results may stimulate the future identification of the NC_2O radical either in the laboratory or in interstellar space.

Finally, we consider the spin contamination and multireference effects of the referenced Hartree−Fock wave functions in the QCISD computations. As shown in Table 1, the $\langle S^2\rangle$ value of 0.7916 for **2** is close to the expected value 0.75 for a pure doublet state, whereas those (0.9487 and 0.9376) for **1** and **4** are slightly larger. This indicates that the spin contamination is not significant for the NC_2O radical, which on the other hand indicates that a single-determinant representation of the wave function is good enough as a starting point for the electronic correlation treatment of NC_2O radical. We should note that the exact QCISD-based wave functions are subject to even less spin contaminations. This is actually confirmed by the further CASPT2(11,11)/cc-pVDZ//CASSCF(11,11)/cc-pVDZ calculations on the species **1**, **2**, and **4**. The obtained geometrical structures (Figure 2) and relative energies (Table 2) are in good agreement with the corresponding B3LYP, QCISD/6-311G(d), G3(MP2)//B3LYP, and G3//B3LYP-based results.

4. Conclusions

A detailed potential-energy surface of NC_2O is theoretically established, involving 9 minimum isomers and 22 interconversion transition states. At the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d)+ZPVE level, the lowest-lying isomer is experimentally known NCCO **1** (0.0 kcal/mol) with bent structure followed by the bent isomer CNCO **2** (16.7). The potential energy surface indicates two isomers, **1** and **2**, and another high-lying species CCNO **4** (99.4) with bent form are kinetically very stable with a barrier of at least 20 kcal/mol. Therefore, they could be observable in the laboratory and in interstellar space. This result is in agreement with their indication of neutralization−reionization mass spectrometry experiments. The possible formation strategies of three isomers in the laboratory and space are discussed in detail. Their molecular properties including the heats of formation, the adiabatic ionization potentials and adiabatic electronic affinities are determined at the higher levels G3//B3LYP, G3(MP2)//B3LYP, QCISD, and CCSD(T) (single-point). We hope that our results may provide useful information for future laboratory and interstellar identification of various NC_2O isomers.

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Supporting Information Available: Figure 5 showing structures of the corresponding cations and anions of the relevant NC_2O isomers at the QCISD/6-311G(d) level. Table 6 showing the calculated spectroscopic properties of the corresponding cations and anions at the QCISD/6-311G(d) level, which are hitherto the most accurate values for them. This material is available free of charge via the Internet at http://pub.acs.org.

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(11) The comparative bond lengths of CH_3CH_3, CH_2CH_2, CHCH, C_6H_6, CH_3NH_2, CH_2NH, CHN, CH_3OH, CH_2O, CO, NH_2OH, NHO, and NO are calculated at the B3LYP/6-311G(d, p) level.

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